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Contacts Between Chalcogenide Glasses, Metals and Semiconductors

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The Director,
Advanced Research Projects Agency,
Washington, D. C. 20301

Contacts Between Chalcogenide Glasses, Metals and Semiconductors

1. General Comments

The two main purposes of the research here described are to elucidate the mechanism of threshold switching, and to explore systems with contact materials which can be electronically altered *in situ*. Public opinion on the status of the switching field as a whole is no doubt governed by reactions to the recent "4th International Conference on Amorphous and Liquid Semiconductors" at Ann Arbor, Michigan, but a consensus of such reactions has yet to be established. As one might expect, a given set of talks can suggest quite different conclusions to different members of the audience. Thus, in the *New Scientist and Science Journal* (London) of September 23, 1971, an (anonymous) contributor reported that thermal theories of threshold switching had carried the day, with electronic models everywhere "on the defensive". To the present writer, the situation appeared in a very different light. At the Ann Arbor conference, purely thermal interpretations of switching were not advocated by anyone. The more successful models presented still suffer from the "thermal" epithet, but do in fact contain electronic terms. They are "thermal" in the sense that they begin with the heat balance equation. However, it is now well understood that thermal terms alone do not yield primary switching characteristics of the kind actually observed. That is why electronic terms have been introduced; not for incidental embellishment,

but in response to essential need. These terms now take the form of a field-dependent electrical conductivity, for which a relatively simple allowance can be made in the equations. Whether they will always be introduced in this particular form remains to be seen. The results given in Section 4, below, make this very doubtful. Even if it were so, it is important to note that the full consequences of a field-dependent conductivity have not yet been included in the calculations. When they are, the electrothermal models (as they should be called) will inevitably look less "thermal" than they now do. Moreover, although electro-thermal models have been remarkably successful in explaining primary switching characteristics, they have not done well with secondary characteristics, e.g. pulse behavior, contact effects, statistical aspects, light sensitivity, etc. For an understanding of the processes involved, these secondary characteristics may be more important than the V-I relationship itself, since the latter could in principle arise in a number of ways. The present writer has prepared his own review of the situation for an article in Nature (London) of which a pre-publication copy is enclosed as Appendix A.

One charge frequently levelled against electronic models of threshold switching is that they are only qualitative, whereas thermal and electrothermal models are quantitative. This is correct, of course, but is by no means an ultimate touchstone of validity. The truth is that the electronic aspects are highly complex, involving a large number of interface and volume parameters. Until more is known about the detailed manner in which charge is injected, trapped, released and transported in the multicomponent amorphous semiconductors, quantitative electronic theories will represent no more than intriguing mathematical exercises. Scarcely a month passes without some new and essential fact about switching being discovered, and this suggests that we have at this stage only a fraction of the

empirical information which would be necessary for the formulation of detailed models.

A good example of how drastically the outlook can change is shown by a recently published paper on the "Forming" of threshold switches [L. A. Coward, J. Non-cryst. Solids 6, 107 (1971)]. Since the earliest days of threshold switching, it has been taken as an article of faith that the current in the OFF-state flows through the entire contact area, whereas the current in the ON-state flows only through a thin filament. The process of switching thus became intimately associated with the process of filament formation. Early results (unpublished and buried in "folklore") seemed to confirm this, because they indicated that pre-threshold currents were proportional to the contact area, whereas ON-currents were independent of it. Coward's recent work shows that this is altogether too simple a view, because of the inevitable "first switch" or "forming" process. He finds that before a new system is <u>ever</u> switched, the OFF-current is indeed proportional to the contact area, but the first switching operation causes a permanent change. It was known from previous experiments that the change leads to a lower threshold voltage for subsequent switching operations. What was not known until Coward pointed it out is that the pre-threshold current after the "first switch" is also <u>independent</u> of contact area. Since the first switching operation lowers the resistance by a known factor and since this permanent modification must be concerned with an area smaller than the smallest contact area examined, one can calculate that a local resistivity increase by a factor of at least 200 must have taken place. It is still an open question whether the ON-state current flows through the same area of cross-section or a smaller one. What is certain is that calculations based on the unmodified bulk properties of the chalcogenide glass would have been wildly misleading. As Coward points out, the parameters which

must be used in models are those of the modified ("formed") filament, and not those of the original bulk film.

Many other examples of the same type could be quoted. A very old maxim is applicable to this field: "Simple solutions should be sought and, when found, distrusted."

2. Problems Under Experimental Investigation

In pursuit of the contract objectives, a number of detailed problems have been under investigation during the last six months:

(a) the nature of the OFF-characteristic, with special reference to time-dependent conductances (current creep) and evidence for space charge effects;

(b) the interaction between successive switching pulses, as a function of film thickness, a problem which concerns not only the understanding of switching processes but all high frequency applications;

(c) the characteristics of switching systems with highly asymmetric electrodes, with special reference to switching delay relationships; (see Appendix B. This material is being prepared for publication.)

(d) differences of switching behavior arising from the "mode of address", e.g. the steepness of applied voltage ramps;

(e) recovery after switching operation, and its relevance to the statistical aspects of threshold switching; and

(f) measurements of self-capacitances as a function of applied bias voltage and film thickness.

Comments on the nature of these problems and on the findings to date are given below, except for item (f) which is still in a very preliminary stage.

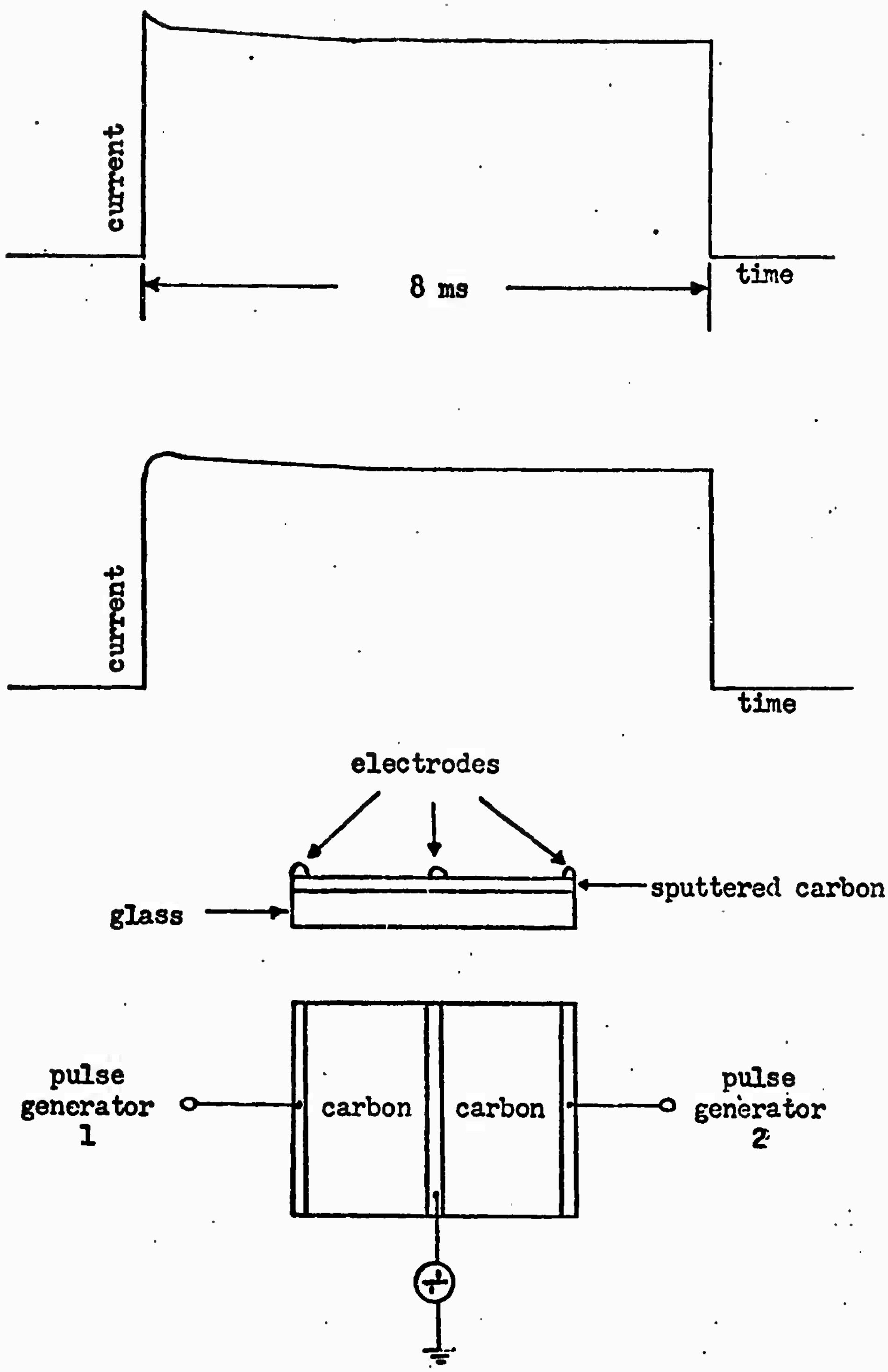
3. Nature of the OFF-characteristic

The field-dependent conductivity terms which have been introduced into the currently popular electro-thermal models make no allowance for time-dependent processes. The presence or absence of such processes is, however, important for our understanding of the phenomena. If the field dependence $\Delta\sigma(F)$ were to arise essentially from the behavior $\Delta\mu(F)$ of the carrier mobility, and one would expect an almost instantaneous effect. If, on the other hand, it were to arise from a field-dependence of the carrier concentration $\Delta n(F)$, e. g. via a Poole-Frenkel effect, then carrier-release and subsequent re-trapping would be expected to lead to current creep at constant voltage. A paper by J. E. Hall [J. Non-cryst. Solids **2**, 125 (1970)], contains results which are of interest in this connection. Hall documents a certain amount of positive creep in the OFF-state close to threshold and visible for 8-10 microseconds after the onset of the constant voltage pulse. For lower applied voltages, the creep effect diminishes sharply until, several volts below threshold, it has virtually disappeared. Hall interprets the shape of his voltage-current characteristics in terms of a space-charge controlled process. However, space-charge controlled currents lead to the expectation of substantial negative creep (while the space charge builds up). This raises two possibilities: (a) that negative creep exists, but only over a short initial period, during which it is obscured by the inevitable "capacitive spike", or (b) that negative creep is a much slower process which becomes prominent at times much longer than 8-10 microseconds. This last possibility can be simply confirmed. When observations are extended over

longer times (e.g. milliseconds), all the units tested here were found to exhibit negative current creep. In some, the negative creep was preceded by a short period of positive creep, with the same time constant as that observed by Hall. In others, no positive creep could be observed (Fig. 1a and b). [On this scale, the capacitive spike is of too short duration to be seen.]

At the other end of the time scale, observations are hampered by the capacitive spike. It was considered that one way of resolving the problem would be by means of a double pulse experiment, since it should be possible to influence the (looked-for) negative creep by preceding 'conditioning' pulses of either polarity. However, Hall's low resistance circuit, though advantageous because it minimized capacitive effects, did not permit the operation of two coupled pulse generators and a new resistive coupling configuration had to be devised. It is shown on Fig. 1c. One of its purposes is to achieve resistive coupling with a minimum of unbalanced stray capacitance, but there is another. It had been found in previous experiments that commercial resistors of the kind that would ordinarily be used in series with switches under test do themselves show a certain amount of negative creep, presumably due to space-charge buildup within them. For tests of this kind, it is therefore imperative to use only highly stable components. The coupling link of Fig. 1c was designed to be so, and tests confirmed its high degree of stability ("creeplessness", to use the local lab jargon) as compared with commercial components.

With these precautions, double pulse experiments on the OFF-characteristic were carried out. Small but measurable polarity effects were observed even at room temperature when the test pulses were preceded by "conditioning" pulses. A preceding pulse of the same (+ve) polarity as the test pulse caused the initial resistance of the system to be in-



(a)

(b)

(c)

FIG. 1. (a) single pulsed OFF-state current in different samples for a long pulse width;

(b) a low capacity "creepless" resistive divider.

creased. A preceding pulse of the opposite (-ve) polarity caused it to be diminished (Fig. 2). [Note, time scale much shorter than in Fig. 1.] The direction of these effects is consistent with space charge interpretations, but their magnitude is small (e.g. $\pm 6\%$, when measured about 1 μ sec after the onset of the voltage pulse). Their magnitude at zero time is presumably much larger but is, of course, outside the present observational range. [As a check, the measurements were repeated, with a creepless, low capacitance resistor in place of the switch. No polarity effects were then observed.]

The results suggest that the above hypothesis is correct, namely that negative creep (sensitive to electrical history) exists but that its initial stages are ordinarily obscured by capacitive spikes. If one were to interpret the effective $\Delta\sigma(F)$ entirely as a change taking place in the bulk material (-and there is no certainty that this is permissible-), then one would have to ascribe it at least partly and perhaps entirely to $\Delta n(F)$. In practice, contact effects will also have to be considered.

Experiments are in progress to check the symmetry of the voltage-current characteristics with greater accuracy than before, there being some indications of rectification.

4. OFF-state and Switching Behavior for Different "Modes of Address"

Among the relationships which are likely to prove of greatest importance for the understanding of threshold switching are scaling relationships, i.e. the variation of electrical parameters as a function of film thickness (see below). However, previous tests had shown that these relationships are not uniquely defined, except for a given "mode of address". Thus, the threshold voltage of a switch differs, depending on whether the switch is being addressed by a square pulse or by a ramp or by a sine wave.

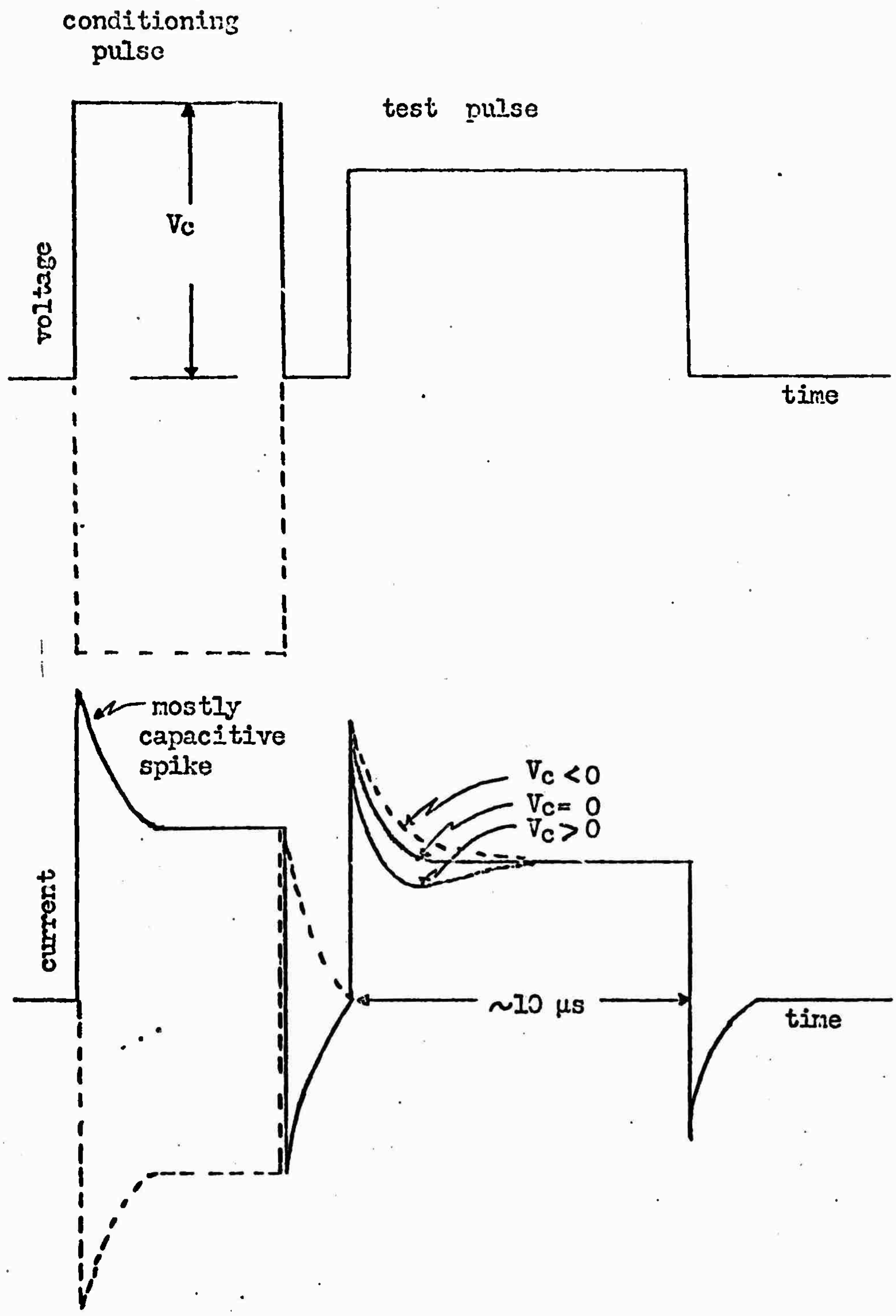


FIG. 2 Double pulse experiment; current and voltage in the OFF-state.

It is therefore important to examine these systems by means of linear ramp voltages of varying slope, and an investigation along such lines has been started. A suitable ramp/generator (based on an operational amplifier) was constructed from a design suggested by R. Shaw. A preliminary set of results is shown in Fig. 3. It compares the voltage-current relationship up to threshold for rectangular pulses of 6μ sec duration (total rise-time of the order of 0.1 microsecond) with the corresponding results of slow ramp measurements.

Currents observed under ramp conditions, include the c(dV/dt) term arising from the stray and specimen capacitances c. The true specimen current is therefore slightly smaller. The stray and specimen capacitances can be independently measured, and a correction for the displacement current can thus be made. The direction of this correction is, of course, to increase the difference between pulse and ramp results. The ramp measurements (which would allow time for possible heating effects) yield lower currents, not higher currents as would be expected on the basis of a thermal hypothesis. Nor are the differences associated in any way with the inherent switching delay. For the rectangular pulses used, this is only about 3 microseconds, in which time the expected ramp overshoot would be quite trivial, compared with the observed differences. By going back and forth between ramps and pulses, it can be ascertained that the internal modification caused by ramps is not of a permanent nature. The existence of a genuine "mode of address effect" of an electrical nature, is therefore confirmed. A paper on this subject is in preparation.

5. Scaling Problems

In view of the importance of scaling relationships, an extensive series of measurements has been initiated, in the course of which thresh-

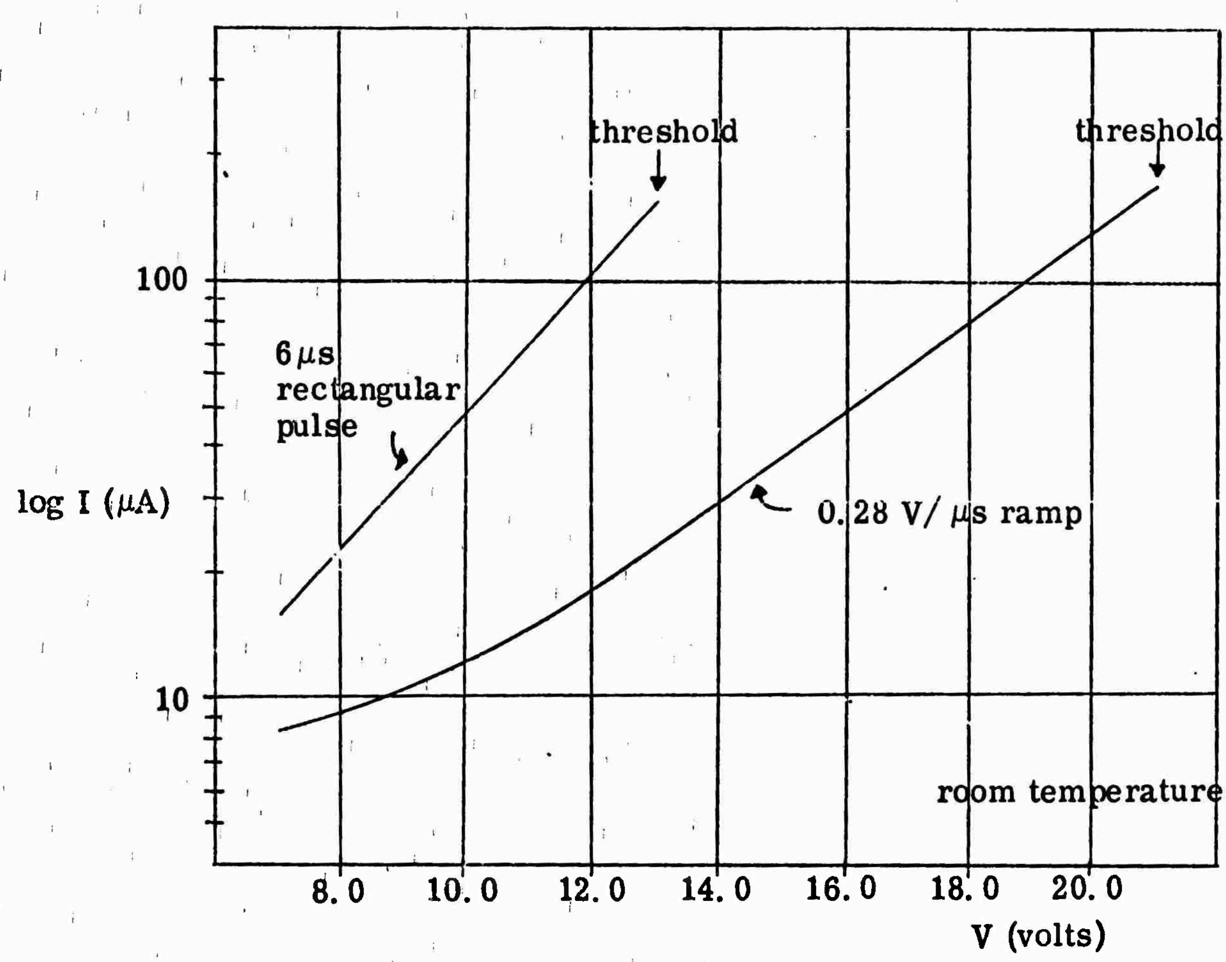


FIG. 3 Effect of "mode of address" on the pre-threshold voltage-current characteristics. Capacitive current correction negligible in this case. [Note that the threshold voltage is higher for the ramp signal than for the pulse. However, this relationship has a maximum: for slowest ramps the threshold voltage is actually lower. Note also identical threshold currents.]

old voltage, pre-threshold V-I characteristics, frequency cut-off and the temperature dependence of these parameters will all be measured as a function of film thickness. For this purpose films of varying thickness will be deposited by sputtering on to polished pyrolytic graphite electrodes. Preliminary results have already shown:

(a) that the resistance at threshold increases much more rapidly with film thickness than the threshold voltage itself, and

(b) that the frequency cut off shifts towards lower frequencies as the film thickness increases. However, it is known (see Appendix B) that thickness is not the only essential parameter in this relationship.

A more detailed report will be provided on completion of the experiments.

6. Recovery Processes

There are many aspects of switch behavior involving internal changes which proceed at a rate much slower than that discussed above. It has been noted, for instance, that the switching delay t_D (under square pulse operation) depends on the repetition rate, even when that rate is very low, as schematically shown on Fig. 4a. This suggests that the physical parameters of the system recover slowly after each switching operation. One such parameter is the OFF-state resistance. Figure 4b shows its behavior following a switching event, when monitored at a negligible applied voltage. The resistance increases by almost two orders of magnitude within about a microsecond, i. e. within the time in which the threshold voltage V_{TH} is known to recover. After that, the resistance increases more slowly by almost three orders of magnitude for about 1 second. Even at longer times, there remains a detectable drist, though it is then very small.

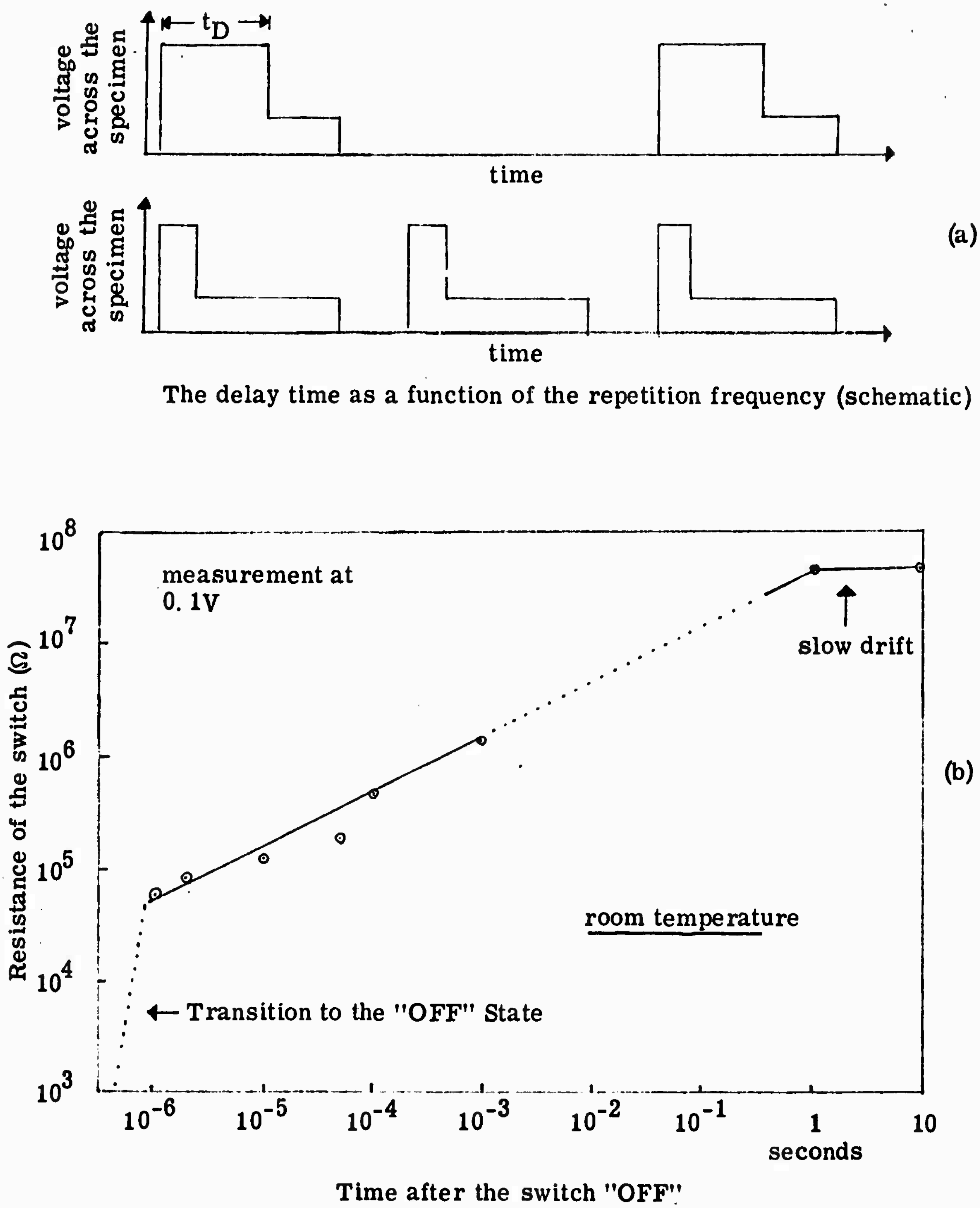
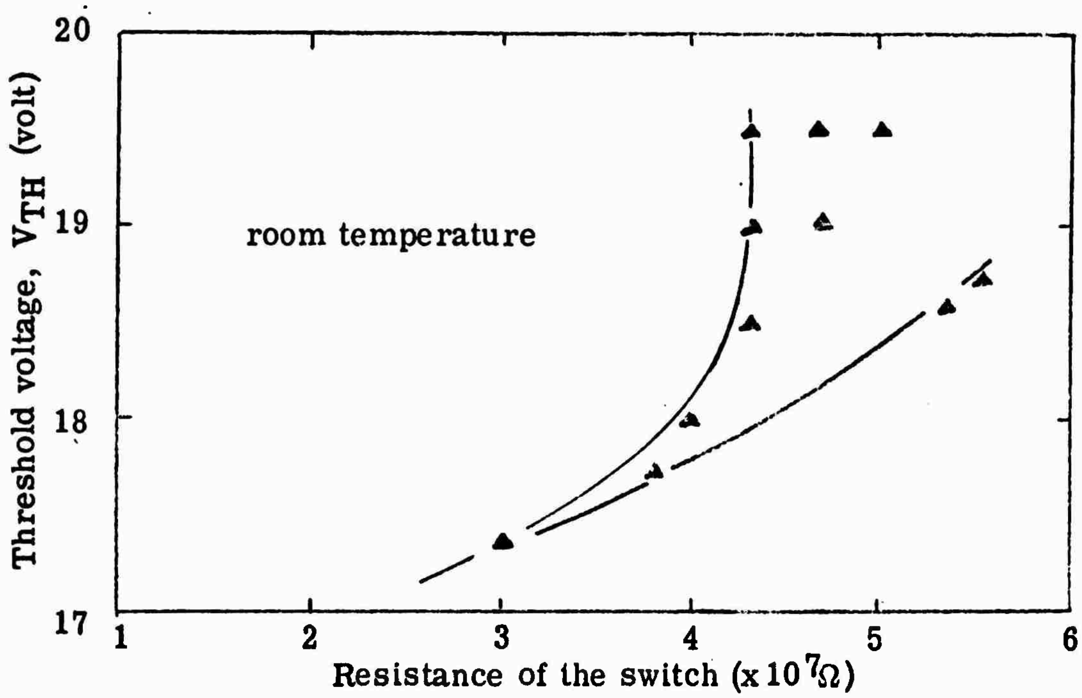


FIG. 4 Recovery processes.
(a) effect of repetition frequency on switching delay;
(b) resistance recovery (measured at very small applied voltage).

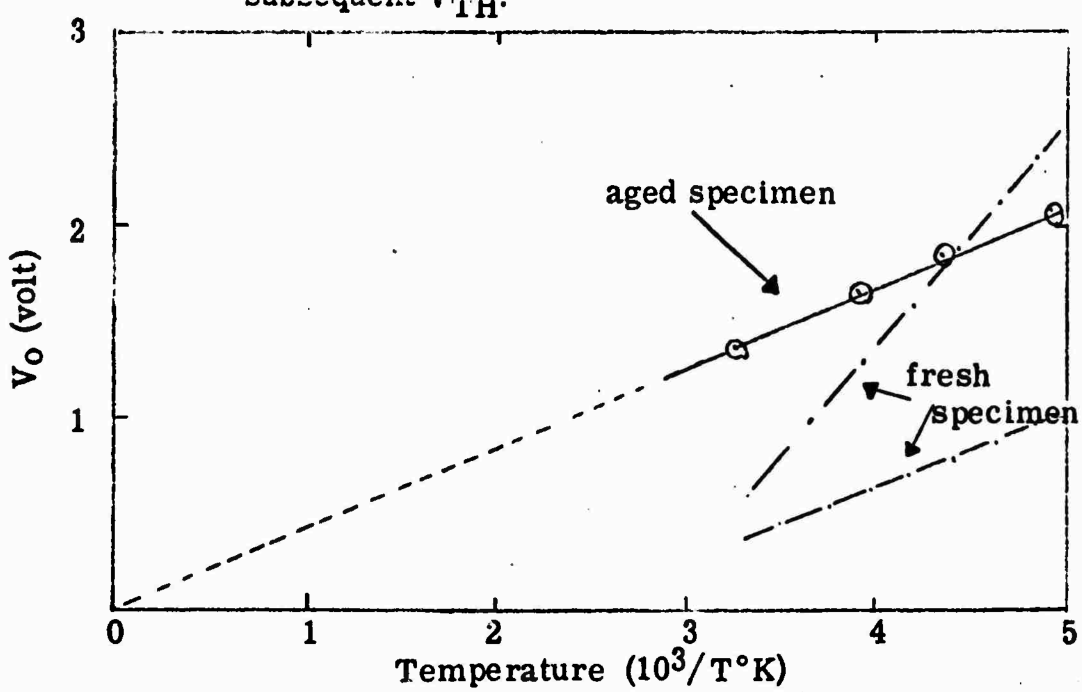
This behavior has an important bearing on the outcome of repetitive switching experiments. When the system is addressed by pulses and the pulse repetition frequency is changed between (say) 1 per second and 10^5 per second, each frequency is associated with a particular stage of the recovery, of which the varying resistance and a corresponding switching delay are merely two outward symptoms. Double pulse experiments have already shown that we are not here concerned with thermal effects, even at the highest repetition rate; at the lowest, such an interpretation is of course a priori implausible.

When a system is switched at minimum voltage (i. e. without intentional overvoltage), the switching delay t_D is the subject of a statistical variation, as noted in previous reports and elsewhere. Its interpretation has always been a difficult problem. In principle, there are two possibilities: (a) the statistical behavior could be inherent in the excitation process, or (b) it could be a consequence of fluctuations occurring during recovery. Neither concept is actually simple, and before elaborate models are worth developing, it is important to identify the origin of the effect as between (a) and (b). The quasi-final resistance values shown on Fig. 1b have been found to exhibit a spread of 8-10% when measured after successive switching events. Why this spread occurs is not yet clear. The immediate question was whether it has anything to do with the time delay statistics. Accordingly, OFF-state resistances were monitored and the threshold voltages experienced by subsequent switching events noted. Results are shown in Fig. 5a. There is evidently a correlation between resistance after recovery and subsequent threshold voltages, though not a one-to-one correlation. When successive measurements are carried out at constant applied (pulse) voltage, the statistical variations of OFF-state resistance correspond to statistical variations of overvoltage and thus of t_D. The conclusion is that the origin of the statistical time delay is at least in large part associated



The relation between the resistance of the switch and subsequent V_{TH}.

(a)



(b)

FIG. 5 Secondary switching characteristics.
(a) correlation between pre-threshold resistance and threshold voltage;
(b) the dependence of V_o on temperature (see page 16).

with the recovery process. The mechanism of the recovery itself remains to be ascertained. Carrier release from traps, ionic migration, and crystallization processes may be involved. Meanwhile, it should be noted that the changes here discussed, though important for an understanding of mechanisms, are small, and would not ordinarily affect operational performance.

The complicated nature of the system can also be judged by reference to the empirically established relationship

$$t_D = t_{Do} \exp(-V/V_o)$$

between the switching delay t_D and the applied voltage V. In this equation, V_o is a constant which still calls for a detailed interpretation. A knowledge of its temperature dependence is important in this connection. In the ordinary way, one might expect V_o to be proportional to T, the temptation being to equate it to kT. However, the experiments show otherwise. In aged (frequently exercised) specimens, V_o is closely proportional to 1/T, as Fig. 5b demonstrates. This makes the above equation more enigmatic than ever! In fresh specimens the temperature dependence is more complicated (shown by the broken lines). Fresh specimens become 'aged' in the course of several hundred operations.

All the above comments relate to unidirectional experiments. Transient polarity effects can be observed when the applied voltage is suddenly reversed. As a result, all manner of composite effects can be observed when switching systems are tested by hybrid procedures. Their disentanglement is a long and not necessarily an informative process. There is really only one important question: are these long-term effects inherent in the operation mechanism of the switch or are they incidental (additional) phenomena. At this time, we are inclined to the latter view.

7. Note on Personnel

In addition to the Principal Investigator, Dr. S. H. Lee (Research Associate), Mr. D. Burgess (Graduate Assistant) and Mr. R. W. Pryor (Graduate Assistant) have been employed on the contract, with Mr. G. J. Vendura, Jr. (Graduate Assistant) also involved, but not paid by contract funds.

APPENDIX A
(In print)

Amorphous Semiconductor Switching

by

H. K. Henisch

A status report, following the
4th International Conference on Amorphous and Liquid Semiconductors,
Ann Arbor (August 9-13),
prepared for Nature (London).

September 1971

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Amorphous Semiconductor Switching

The subject of switching in amorphous semiconductors owes its present vogue to two aspects: (a) the possibility that switching phenomena might somehow throw new light upon the fundamental nature of amorphous matter, and (b) the appearance of new solid state devices of a kind not feasible with conventional (crystalline) semiconductors. Since amorphous semiconductors as such have been with us for as long as the crystalline variety without causing much stir [except in the context of xerography], it is safe to conclude that the new interest in (a) owes a great deal to (b). Sentiments widely expressed at a recent international conference* bear this out. Nor is this surprising, because new devices and their applications have already become a reality, as could be seen from a series of demonstrations by S. R. Ovshinsky (Energy Conversion Devices, Inc.). With (b) above at least partially fulfilled and further new devices on the horizon (Nicolaides and Doremus, Hamakawa, Yoshida and Yamanaka, Ovshinsky and Klose), the question is: what becomes of (a), and on that point some further clarification is desirable. Though many amorphous materials are of interest in this context, the present comments are limited to switching systems based on multicomponent chalcogenide glasses, partly for the sake of brevity and partly because only such systems have so far reached the level of practical usefulness.

The principal facts are well known. When thin (e.g. 1μ) glass films between suitable (non-reactive, non-diffusing) electrodes are electrically examined, their voltage-current characteristics are found to be as shown by the full lines on Fig. 1. The OFF-state is stable; the ON-state metastable, requir-

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*4th International Conference on Amorphous and Liquid Semiconductors, Ann Arbor, Michigan, August 9-13, 1971. The proceedings (with all the contributions mentioned in this review) will be published in a forthcoming volume of the Journal of Non-crystalline Solids.

ing at least I_{MH} (the "minimum holding current") for its maintenance. In this form the system is called an ovonic threshold switch. As long as the switching cycle is performed sufficiently fast (e.g. with megacycle frequency), such characteristics are observed for all systems, irrespective of glass composition and thus of the glass transition temperature (T_g). However, in films made of low T_g glasses, the ON-state can be stabilized by prolonged power dissipation at the points P_1 or P_2. The process requires 2-15 msecs, depending on the applied voltage and series resistance. When such a 'set' pulse has been applied, the V-I characteristic in the ON-state passes smoothly and permanently through the origin. In this form the system is called an ovonic memory switch. Whereas the current below threshold is proportional to the contact area, the ON-current is independent of it. This means that the ON-state prevails not over the whole volume of the device but only within a filament. Memory switches can be conveniently arranged into random access arrays ("Read Mostly Memories") and are used for complex information storage. Such units are described by the endearing term 'non-volatile' because the impressed information (i.e. the existence of the ON-state) does not depend on the continued presence of power supplies. Because memory as such is no virtue without a corresponding process of controlled forgetting, a 'reset' procedure is also called for. This again takes the form of a current pulse (e.g. 150mA for 6μsecs) but with a sharp trailing edge and a higher rate of energy dissipation than that of the 'set' pulse. The 'reset' pulse therefore involves considerably higher filament temperatures, well above the liquidus temperature of the glass. The sharp trailing edge implies quenching, in the course of which the original OFF-state is restored. It is also known that filament formation is accompanied by crystallization processes. In glasses which contain substantial amounts of Ge and Te, the filament consists mainly of degenerate Te with a metallic-type conductivity, with highly doped GeTe as a possible second phase among the Te crystallites. In the

state of electronic disequilibrium involving broken bonds, or (most probably) both? This is certainly one of the points on which controversy tends to flare: the mechanism of threshold switching.

A good deal of evidence indicates that typical ON-state filaments have a cross-sectional area of the order of about $5.10^{-8}cm^2$. With ON-currents of (say) 10mA, this implies current densities of the order of $5.10^5 amps/cm^2$, and under such conditions, the notion of completely isothermal operation becomes implausible. Energy is being dissipated, and since the medium is highly temperature sensitive (by virtue of its mobility gap), this is unlikely to be without electrical consequences. The question, therefore, has never been whether heating effects are absent, but whether their role is incidental (e.g. as in a transistor) or necessary and sufficient (e.g. as in thermistor operation) or, perhaps, significant (in varying degree) but insufficient. In connection with the last possibility, it is immediately clear that the role of self-heating must increase with increasing film thickness. Because thermal and electronic processes can both lead to filament formation, such differences of mechanism may not show themselves at all clearly in the shape of the (primary) V-I switching characteristics.

Because some heat development is inevitable, it was natural and reasonable that attempts to explain ovonic threshold switching should concern themselves first with thermal models. However, though the concept of thermal breakdown has been with us for a long time, its detailed implications are only now beginning to be understood. Models which might be described as 'simple and <u>purely</u> thermal' are those which contain $\sigma = \sigma_0 \exp(-\Delta E/kT)$, or some such term, as the only critical assumption. Such systems can certainly yield negative resistance behaviour (in thermistor fashion) but, as is now known, never V-I relationships of the kind shown on Fig. 1, it being characteristic of threshold switches that the current cannot be stabilized in any way between the threshold points and points P_1 or P_2 (see Conference papers by Kaplan and

course of the 'reset' pulse, the crystalline regions are redissolved and subsequently quenched back into the amorphous state. At Ann Arbor, Cohen, Neale and Paskin gave a detailed and convincing account of this process. Whereas the term "Read-Mostly" is undoubtedly diplomatic parlance for "Write-Rarely", the number of times a switch can be activated is not actually small. Individual units (as opposed to arrays) are now being routinely "exercised" with over a million switching cycles, more than sufficient for the intended applications, e.g. micro-programming computer memories, machine instructions, telephone dial codes, etc. The memories are interrogated ("read") by much lower voltage signals, and the number of read-cycles is therefore virtually unlimited.

The general principle of the memory switch is therefore well understood, but intriguing and important questions remain. How, for instance, does the crystallization come about? Is a homogeneous separation into two glassy phases originally present in submicroscopic form and does one of these phases later crystallize into the conductive path. (Conference opinions: Roy <u>et al</u>, Feltz <u>et al</u>: yes; Moss <u>et al</u>: no.) Alternatively, do the crystals form by nucleation within an originally single phase medium? If so, what is the nucleation mechanism and what, if anything, does it owe to electrolytic (or, at any rate, polar) phenomena observed on some of the larger electrode systems? By now, it is strongly felt that these questions cannot be answered categorically for all systems, but must be examined separately for various families of alloys. There remains also the most important question of them all: is the high temperature reached during the setting pulse a sufficient condition for the stabilization of the ON-state or only a necessary one? The last question arises from the fact that memory switching always <u>follows</u> threshold switching. The stabilization occurs, therefore, when the system is in its (threshold) ON-state, and this makes it important to know the real nature of that state. The choice: are we dealing simply with a hot filament or with a

Adler, and by Popescu and Croitoru). To achieve such characteristics on a thermal basis, it is necessary to postulate a lateral instability of the current distribution, i.e. to envisage filament formation, arising from some secondary cause. It does not matter in principle, whether the filament is provoked by a thermal or an electronic fluctuation; its formation redistributes the current and thereby leads to switching. However, in order to achieve reasonable agreement on points of detail (e.g. shape of the ON-characteristic, scaling of threshold voltage with film thickness, etc.), it is necessary to make at least one additional assumption: that the electrical conductivity of the medium is field dependent. On this basis, a remarkable amount of success has been achieved (e.g. Cohen and Kroll, Popescu and Croitoru, Robertson and Owen) in explaining the primary switching characteristics (Fig. 1). These models, which differ on points of detail, should always be called 'electro-thermal' to express and maintain their crucial distinction from simple thermistor action.

The next questions are: (i) Does a field-dependent conductivity correspond to established facts? (ii) What are the features which the present electro-thermal models cannot -- or, perhaps not yet -- explain? (iii) How can such models be further developed and refined? (iv) Are there alternative approaches which the available facts leave open? Each question merits extensive discussion, but only brief answers can be suggested here, and these must necessarily reflect the writer's personal assessment of the situation.

(i) A field dependent conductivity $\sigma(F)$ is a plausible assumption (though, of course, no more) pending direct experimental verification in the materials concerned. The corresponding experiments are not easy, because electrode effects which could simulate a $\sigma(F)$ must be rigorously eliminated, and because isothermal conditions must be assured, despite the presence of high

fields. If $\sigma(F)$ could be shown to be a reality, it might arise from one of two causes (or both): from a field dependent mobility or from a field dependent carrier concentration (via Poole-Frenkel). The latter case concerns, of course, an electronic disequilibrium situation and would at once involve us in questions of lifetime, trapping and space charge. Moreover, it is primarily through $\sigma(F)$ that electro-thermal models envisage switching to be related to the basic bulk properties of the material concerned. Because of the key position which the $\sigma(F)$ assumption holds in electro-thermal switching theories, its experimental exploration has become one of the most important pending tasks.

(ii) There are, indeed, features which the present electro-thermal models cannot or, at any rate, do not satisfactorily explain. Most of them come under the heading of secondary characteristics. Figure 2 gives a digest, schematic and incomplete but broadly representative of the situation. To these results one must add some highly significant observations by Regel and co-workers on high temperature (e.g. 500-600 C) switching in liquid semiconductors of widely varying conductivity.

(iii) The present electro-thermal models neglect all contact effects [e.g. arising from barriers, injection, etc.], all space charges [including those implied by the calculated non-linear field distribution] and their transport during switching, all possibilities of electronic disequilibrium in bulk [whether arising from impact ionization or the Poole-Frenkel effect or any other effect responsible for $\sigma(F)$], all trapping phenomena [including any relationship between switching and trap distribution which may exist in these materials]. There is, therefore, both need (see above) and opportunity for further refinement, all of which will tend to emphasize the <u>electro-</u> in "electro-thermal".

(iv) Past attempts at interpretation began with purely thermal concepts and proceeded by introducing electrical terms when needed. (Thus, Robertson and Owen refer to "electronically assisted thermal breakdown".) Because switching as such can in principle be obtained by purely electrical means, e.g. as theoretically analyzed by Mott, van Roosbroeck, Lucas and others (pre-conference work) and observed also in various crystalline semiconductor systems, the opposite approach is also feasible, namely to begin with electrical concepts and to proceed by introducing thermal correction terms. Because of the complicated band relationships involved, most (though certainly not all) such attempts have in the past been only qualitative, but there is every reason to believe that the situation can and will change. The question: "Which is more important, the electrical or the thermal contribution?" may well turn out to have no precise meaning. It is already judged to be less important than it once was, partly because the calculated filament temperatures have been steadily decreasing (e.g. Cohen and Kroll) and partly because it is now known that threshold switches can withstand an astronomical number of switching cycles without sign of damage. On the other hand, every time the threshold switch is judged to be cooler than previously believed, the problem of interpreting the memory switch in purely thermal terms increases in severity, one of the poignant dilemmas of the day!

It cannot be said that our understanding of threshold switching has reached a stage which would permit the phenomenon to be used as a "tool" for the direct exploration of the amorphous state. On the other hand, this very possibility has been on the horizon since the non-thermal aspects of switching have begun to be recognized, and it remains a reasonable hope that switching

research will do for amorphous semiconductors what transistor research did for the crystalline variety.

Figure Captions

FIG. 1 Primary switching characteristics; threshold and memory models. Threshold voltage $V_{TH} \sim$ prop. to film thickness.

FIG. 2 Secondary threshold switching characteristics.

(a) $(V_{TH})_B$ independent of total energy dissipated by the A-pulse and, over a wide range, also independent of A- current in the ON-state.

(b) Lengthening of switching delay through pulse reversal, typical of various polar effects observed at low temperatures (only).

(c) Asymmetrical switching characteristics of a germanium-glass-graphite system (glass thickness $\approx 0.2\,\mu$); asymmetries reversed for n-type and p-type substrates (Henisch, Pryor and Vendura).

(d) Transient ON-characteristic, as determined via temporary (e.g. $0.1\,\mu$sec) excursions from the point V_{ON}, I_{ON} (Henisch, Pryor and Vendura).

(e) Statistical aspects of switching (Lee, Henisch and Burgess).

(f) Q_o proportional to film thickness (Haberland and Stiegler).

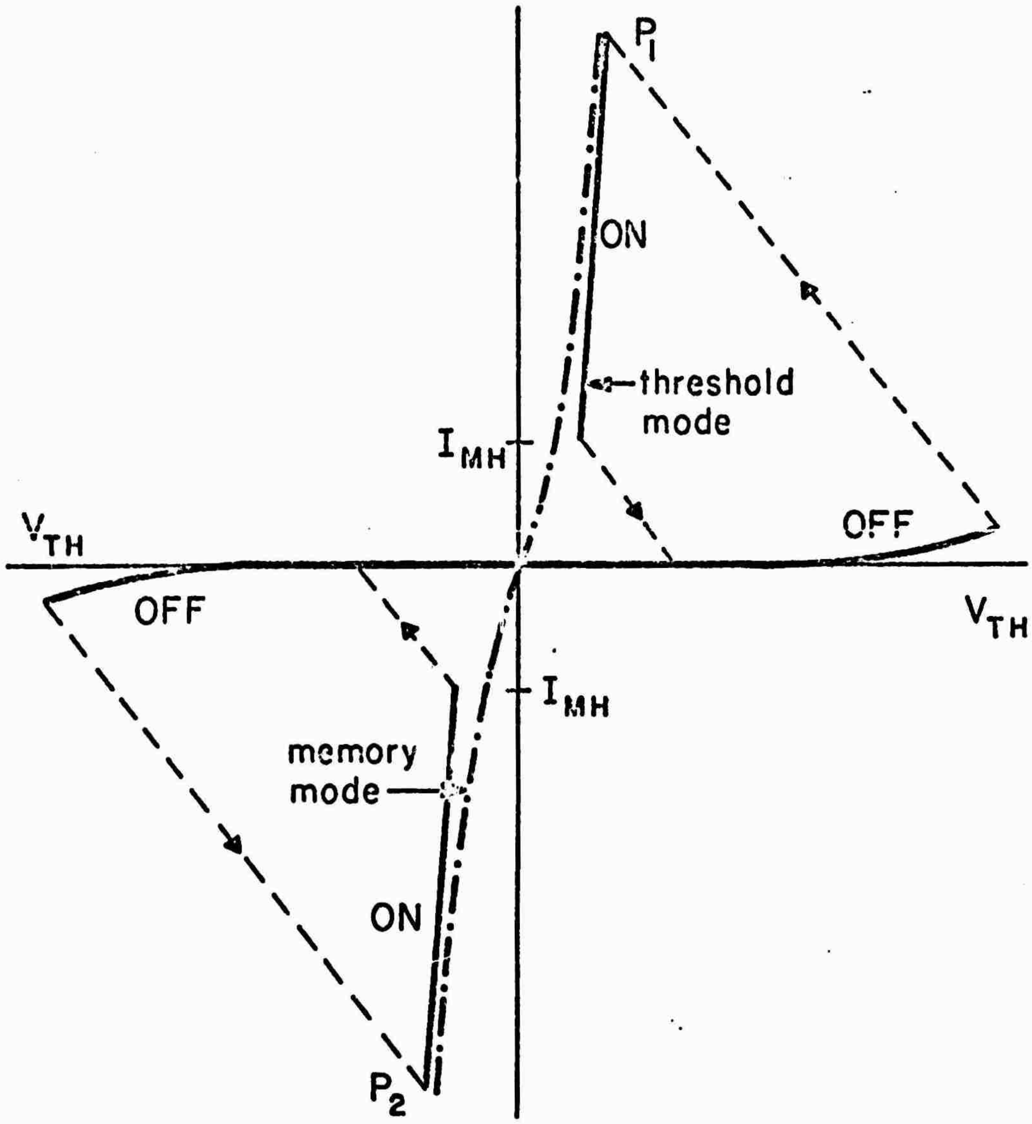
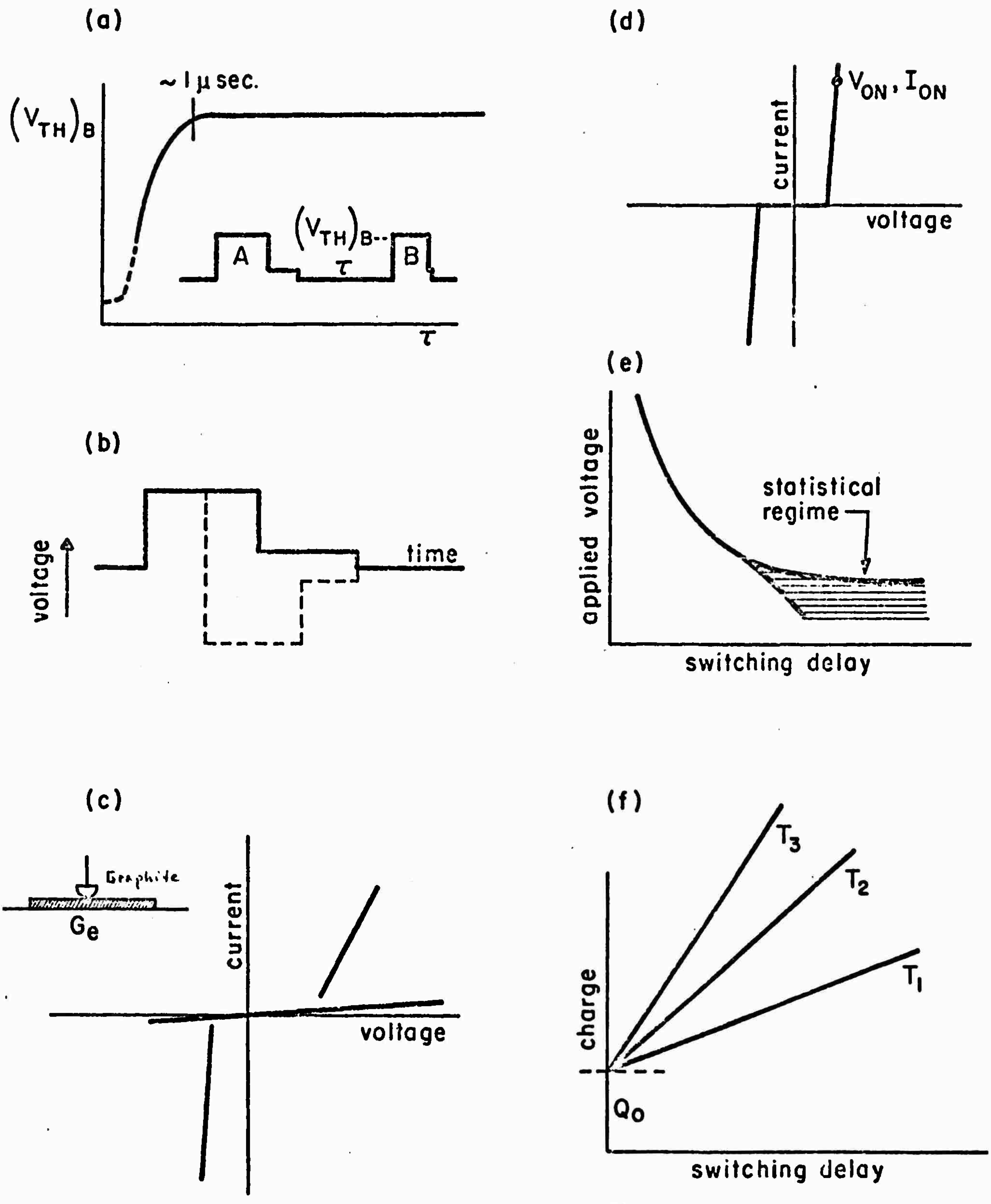


Fig. 4


(a)
~1 μsec.
$(V_{TH})_B$
A
$(V_{TH})_B$
τ
B
τ
(b)
voltage
time
(c)
Graphite
G_e
current
voltage
(d)
current
V_{ON}, I_{ON}
voltage
(e)
applied voltage
statistical regime
switching delay
(f)
T_3
T_2
T_1
charge
Q_0
switching delay

33

Fig. 2

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Behavior of Amorphous Semiconductor Films Between Asymmetric Electrodes

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The interpretation of switching phenomena in amorphous semiconductor films and particularly in the multicomponent chalcogenide glass alloys depends critically on the role assigned to the electrode interfaces. The first purely thermal theories advanced (1-5) and even the more modern electro-thermal models (6-8) assign no such role, in harmony with the practical experience that the primary switching characteristic (i. e. the voltage-current relationship) is not sensitively dependent on the electrodes, as long as plausibly inert materials (e. g. graphite, tungsten, molybdenum) are used. However, the significance of this observation is in doubt, because important electrode effects have been noted in other contexts, e. g. by Altunyan and Stafeev (9), and by Pryor, Henisch and Vendura (10, 11). In particular, chalcogenide glass films between sufficiently asymmetric electrodes show asymmetric switching behavior (11) of a kind not interpretable in thermal terms. Such observations have been made on systems consisting of a crystalline germanium substrate, covered with a flash-evaporated film of $Te_{40}As_{35}Ge_{7}Si_{18}$ and tested with a counter-electrode of pyrolytic graphite or tungsten. The corresponding voltage-current characteristics were generally of the type shown in Fig. 1, however, with substantial variations from point to point. Some points do not show stable switching at all, and there is as yet no understanding of the local variations.

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For sufficiently high current levels, rectification was one aspect of the observed behavior, but it was concluded from an inspection of the voltage-current characteristics that a simple model involving a contact rectifier in series with a non-interacting, conventional threshold switch could not account for the observed behavior. Since this interpretation has an important bearing on the role ascribed to contact interfaces, it was in need of a more direct check, and this has since been provided. Figure 2 shows frequently encountered forms of the voltage-time relationships on n-type Ge substrates. The rectification and its reversal as between (a) and (b) is again evident, but it will be noted that the time relationships are entirely different for the two directions of current flow. There is therefore no question of simple scaling, the only process which a non-interacting rectifier would be capable of superimposing on switching behavior. On the contrary, the entire sequence of events is different in the two directions of current flow, and the results leave no doubt about the fact that this difference is associated with the nature of the electrodes. While the detailed form of this behavior is not yet properly understood, the notion that germanium and graphite electrodes have different injection efficiencies is in harmony with the observations. The slow voltage drop (implying a conductance increase) on Fig. 2b is highly reminiscent of experiments with optically injected carriers (12). The time required to reach the steady state being interpreted as the time required for injected carriers to penetrate the entire film thickness.

The fact that the two mechanisms of current flow are different in the two directions is also shown by their response to illumination. For a film on an n-type Ge substrate, this is illustrated by the dotted lines on Fig. 2a. The low resistance state in the negative direction is independent of light, and of the applied external voltage. In view of this, and because the low resistance state is reached sooner when the applied voltage is higher,

this condition corresponds most closely to the ON-state of conventional threshold switches. However, in the case shown there is no critical negative threshold voltage at which the resistance change begins to show itself (as long as the applied voltage exceeds the level corresponding to the low resistance state). In the positive direction, the behavior is very different; there is a well defined threshold voltage below which the sudden resistance change is not observed. For amorphous layers on p-type Ge substrates, the results are somewhat similar, but with reversed polarities. However, no light effect was observed for negative applied voltages, and for positive voltages the resistance was light dependent (Fig. 2b) throughout. (Compare Fig. 2a.)

There is a second important respect in which the behavior of symmetrical and asymmetric systems differs. For conventional (symmetrical) threshold switches, it is well known (13, 14) that a switching operation <u>reduces</u> the threshold voltage experienced by a subsequent switching process, if the time interval is of the order of a microsecond or less. The switch "remembers" a previous operation. From opposing viewpoints it has been argued that this temporary memory is electronic in nature or, alternatively, that it is purely thermal. Figure 3 gives results of a double-pulse experiment carried out on an asymmetric n-type system as described above. In the upper trace, the voltage pulses are about 10 microseconds apart, and each exhibits switching (in the manner shown on Fig. 2a). When the pulses are moved together, without change of applied voltage, the second pulse ceases to switch. There is a threshold voltage <u>increase</u> towards smaller time intervals, instead of the decrease ordinarily observed. This trend persists over at least 9 microseconds, down to 0.5 microsecond, the limit of observation for the test circuit used (Fig. 3b). The increase is found for a substantial number of contact points but not for all of them. What happens at shorter time intervals is not yet known. Meanwhile, it is

important to note that a threshold voltage increase cannot be associated with heating, and must therefore arise from electrical (and probably electronic) causes. The fact that such an upward trend can exist (for whatever reason) also means that the frequency cut-off presently associated with threshold switches is not necessarily an inherent and permanent feature.

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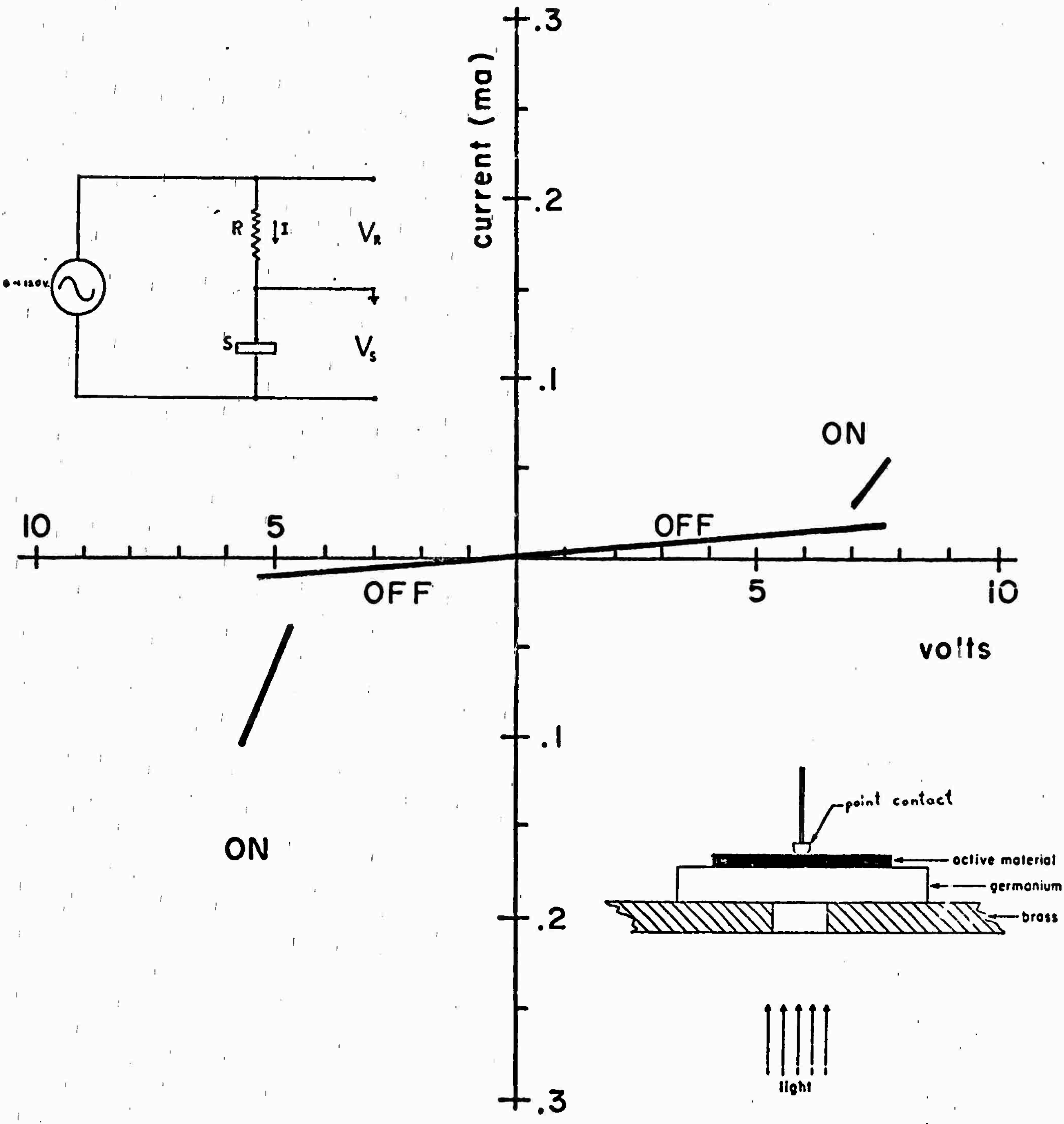

FIG. 1 Switching systems with asymmetric contacts; dynamically tri-stable voltage-current characteristics.

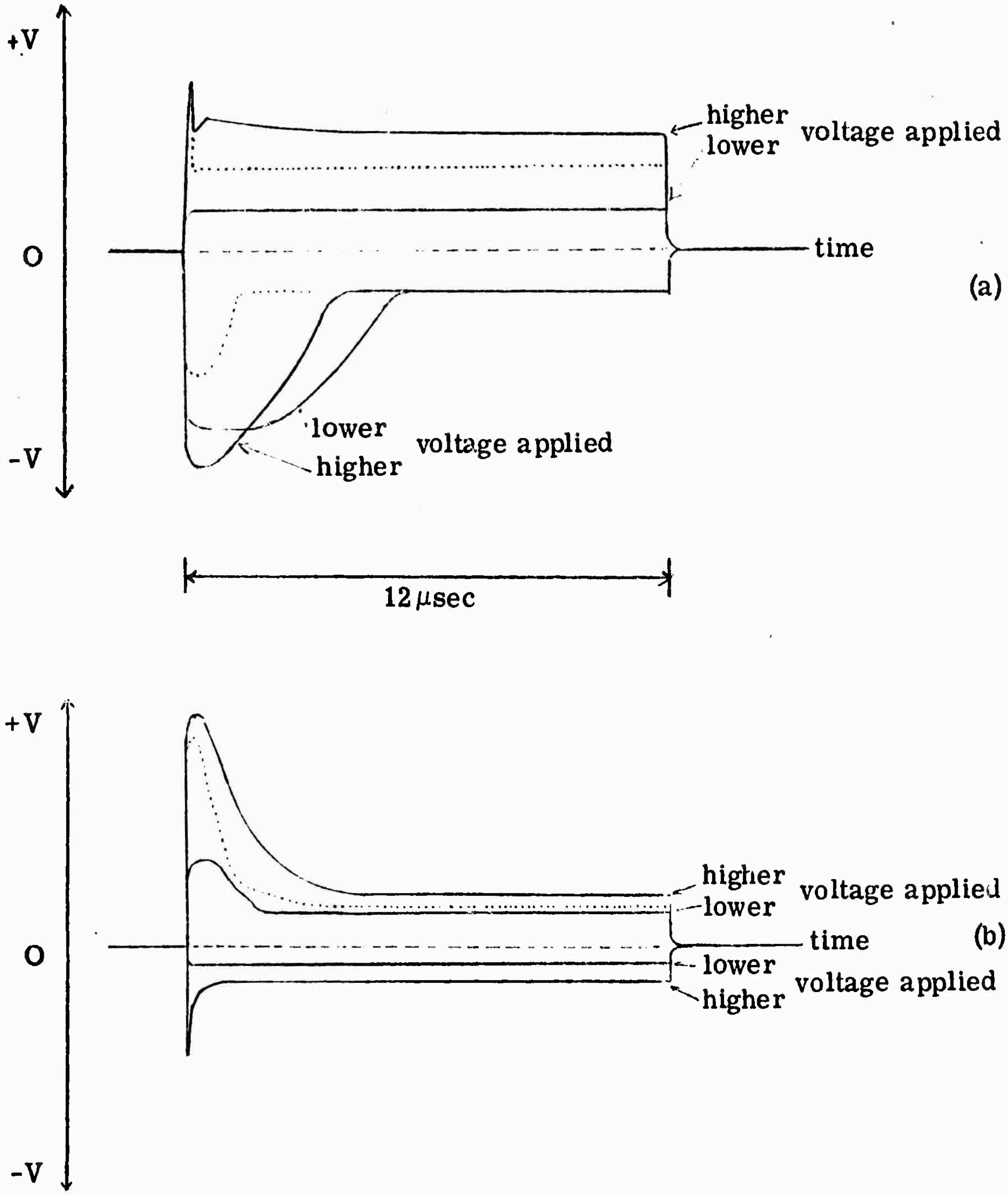

FIG. 2 Voltage-time relationships for switching systems with one tungsten and one germanium electrode.
(a) n-type Ge,
(b) p-type Ge.
Positive direction shows polarity of the tungsten contact.
Dotted lines denote characteristics under illumination.

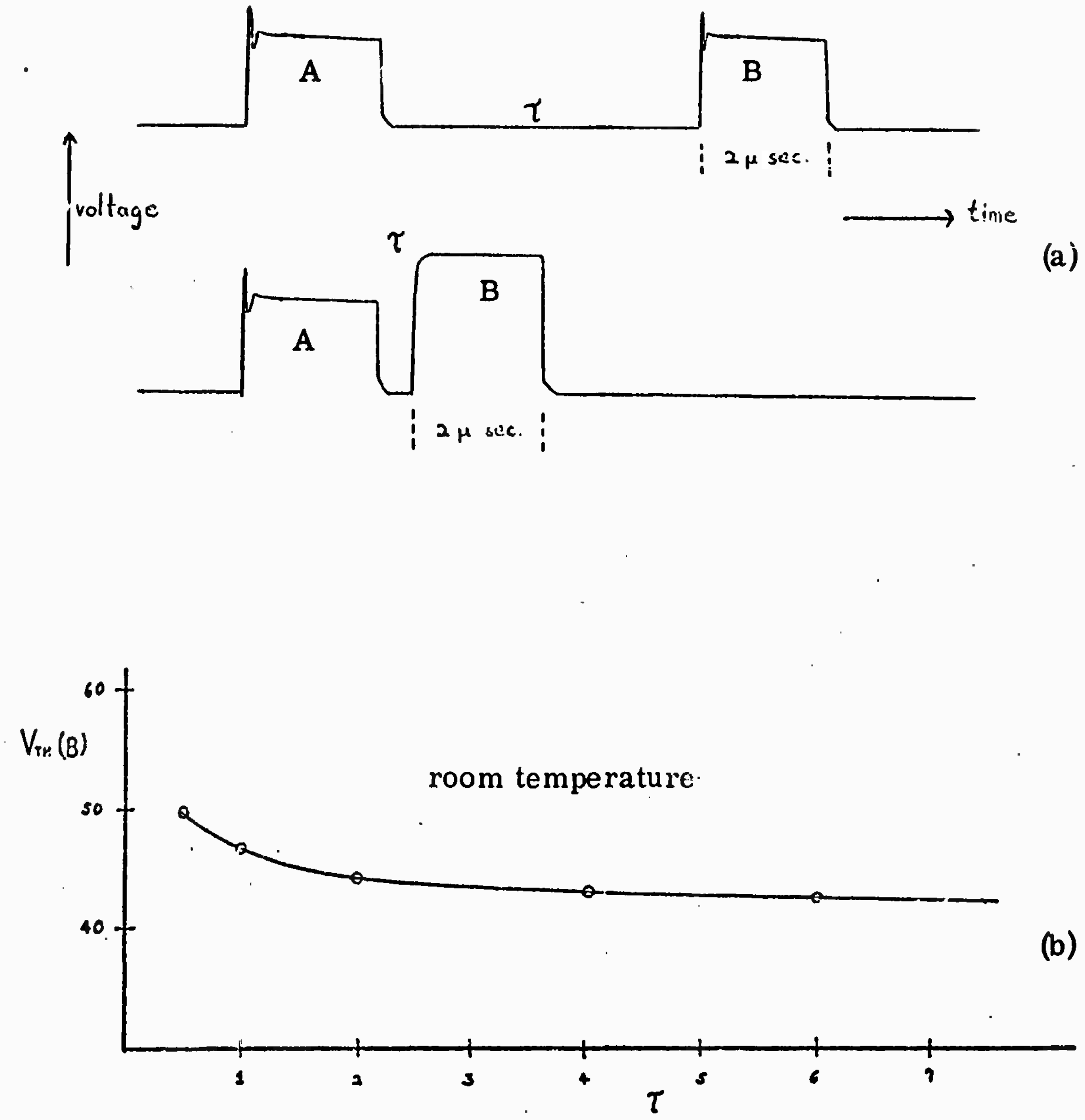

FIG. 3 Double pulse experiments on switching systems with asymmetric contacts (tungsten point contact, n-type Ge substrate).

(a) upper trace: A and B pulses far apart; both pulses switch.
lower trace: A and B pulses close together, with same external voltage applied; B pulse does not switch.

(b) the $V_{TH}(B)$-τ relationship for such a contact point.

Pulse pair repetition frequency: 50 per sec.